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In situ carbon mineralization in ultramafic rocks: Natural processes and possible engineered methods

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Abstract

In this invited review, we summarize the main results of ongoing research on “*in situ*” carbon mineralization in ultramafic rocks, including outcrop studies in Oman (e.g., [1, 2]), investigation of carbon mass transfer in subduction zones from the Oman Drilling Project (e.g., [3–7]), laboratory investigations (e.g., [8–12]) and numerical modeling (e.g., [13–17]) of the pressure of crystallization and reaction-driven cracking, and assessment of the rate, cost and capacity of various proposed methods for engineered carbon mineralization [18, 19].

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1. Introduction

Natural carbon mineralization in ultramafic rocks, particularly in tectonically exposed mantle peridotites, provides striking field evidence for rapid and complete uptake of CO₂ from the atmosphere and natural fluids to form solid carbonate minerals. Such processes – particularly in the oceanic upper mantle near oceanic spreading ridges, the outer rise near deep sea trenches, and in the “leading edge of the mantle wedges” overlying subduction zones – form important reservoirs in the global carbon cycle (e.g., [20]). Formation of weak layers of carbonate minerals, and related, hydrous Mg-silicates such as serpentine, is important in creating and maintaining tectonic plate boundaries. Oxidation and reduction of dissolved carbon species during peridotite alteration may lead to abiotic synthesis of hydrocarbons, and provide an energy source for subsurface, chemosynthetic microbial communities.

Seifritz [21] and Lackner et al. [22] proposed that spontaneous, exothermic, rapid carbon mineralization in peridotite could be harnessed for CO₂ capture and storage. This idea gained credence with experimental confirmation that olivine undergoes carbonation (via $\text{Mg}_2\text{SiO}_4 \text{ olivine} + 2 \text{ CO}_2 = 2 \text{ MgCO}_3 \text{ magnesite} + \text{SiO}_2 \text{ quartz}$) faster than any other abundant, rock-forming mineral [19, 23–25]. Proposed engineered methods may be divided into *ex situ* processes – quarrying and grinding rock reactants, and transporting them to pressure vessels, where they react with fluid at high temperature and a high partial pressure of CO₂ – and *in situ* processes, in which CO₂ is transported by fluid flow along fractures and pores into subsurface rock formations at naturally elevated temperature and pressure. In this paper, we also refer to natural, subsurface carbon mineralization as an *in situ* process.

Nomenclature

<i>Ultramafic</i>	rock containing <45 wt% SiO ₂ and >18 wt% MgO, and/or composed of >90 wt% “mafic minerals”, which are olivine, pyroxenes, amphiboles, and serpentines
<i>Peridotite</i>	ultramafic rock containing more than 40% olivine (aka “peridot”)
<i>Olivine</i>	mineral solid solution between end-members forsterite (Mg ₂ SiO ₄) and fayalite (Fe ₂ SiO ₄); olivine comprises more than 60% of the Earth’s upper mantle, where it is ~ 90% forsterite
<i>Serpentine</i>	hydrous silicate mineral group with Mg-end member Mg ₃ Si ₂ O ₅ (OH) ₄ ; formation of serpentine plus other minerals by hydration of ultramafic rocks is often called <i>serpentinization</i> ; rocks composed mainly of serpentine are called <i>serpentinites</i>
<i>Carbonates</i>	minerals such as <i>magnesite</i> (MgCO ₃), <i>calcite</i> (CaCO ₃) and <i>dolomite</i> (MgCa(CO ₃) ₂); formation of carbonate minerals by reaction of CO ₂ with Mg- and Ca-bearing silicates is commonly called <i>carbonation</i> and <i>carbon mineralization</i>
<i>Listvenite</i>	rock composed of carbonate minerals + quartz + Fe-oxides + Cr-rich oxides or silicates, produced by complete carbonation of peridotite, in which all Mg and Ca combine with CO ₂ , most Fe forms oxides, and all SiO ₂ forms quartz
<i>Quartz</i>	SiO ₂ mineral
<i>Crust</i>	Relatively low density, SiO ₂ -rich, uppermost layer of the solid Earth; oceanic crust is about 7 km thick; continental crustal thickness is variable but averages ~ 36 km
<i>Mantle</i>	Relatively dense, ultramafic layer of the solid Earth, underlying the crust; the upper mantle – from the base of the crust to ~ 410 km depth – is composed of peridotite and contains abundant Mg-rich olivine
<i>Spreading ridge</i>	narrow zone of extension and formation of new, igneous ocean crust between two diverging tectonic plates
<i>Subduction zone</i>	thrust fault at zone of convergence between two tectonic plates where one plate is thrust beneath the other; typically, old oceanic crust is thrust into the mantle
<i>Hanging wall</i>	block of rock overlying an inclined fault plane
<i>Mantle wedge</i>	mantle portion of the hanging wall above a subduction zone
<i>Ophiolite</i>	fragment of oceanic crust and upper mantle – an oceanic plate – thrust onto a continental margin

2. Outcrop studies

Outcrop studies of partially to fully carbonated peridotite provide a range of data; field relationships, whole rock geochemistry, mineral assemblages and compositions, and thermodynamic modeling – that support the hypotheses that these processes are geologically rapid, lead to reduction and oxidation of dissolved carbon species, and involve addition of substantial CO_2 ($\pm \text{H}_2\text{O}$) to form solid hydrates and carbonates, decreasing the solid density, combined with removal of comparatively small amounts of other, dissolved components (review [26]; more recent work, e.g., [27–49]). Peridotite carbonation and hydration (serpentinization) thus causes substantial increases in solid mass and volume. Such changes could lead to negative feedbacks – clogging porosity and armoring reactive surface area – but geologic examples of complete carbonation and serpentinization indicate that these feedbacks do not always limit the extent of reaction. The supply of CO_2 to reactive mineral surfaces via fluid flow along new fractures, which form during peridotite alteration, clearly plays a major role in the carbon mineralization process. Carbonate minerals in altered peridotite commonly form veins in fractures. Textures record coeval carbonate deposition and expansion of the rock volume. In fully carbonated peridotites (listvenites), quartz as well as carbonate veins are present, vein densities are high, and the rock matrix between veins is 100% carbonate + quartz + Fe-oxides + minor Cr-bearing minerals.

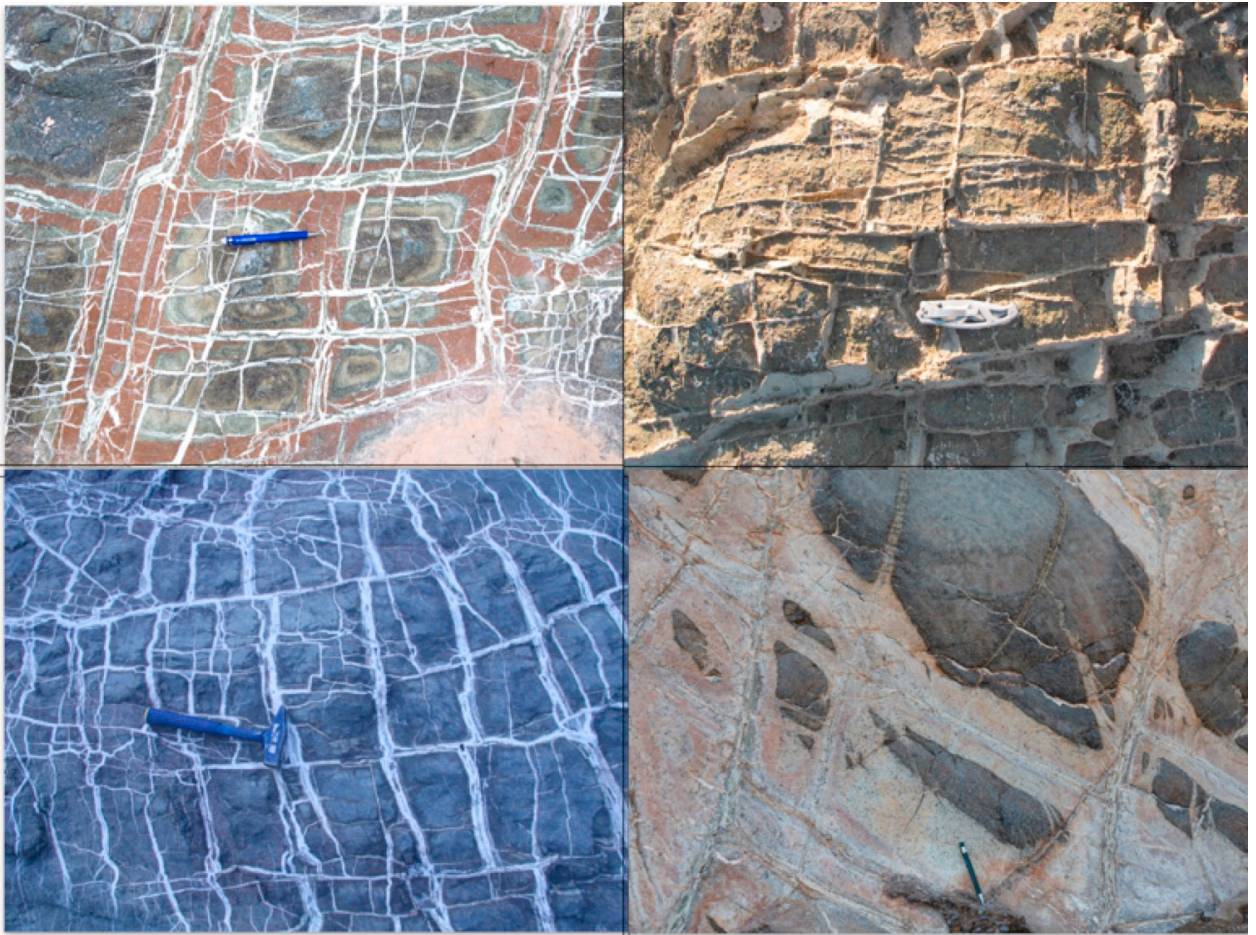


Fig. 1. White carbonate veins in partially serpentinized peridotites in Oman. Two left hand images: Kelemen pers. comm. 2017; top right: Kelemen and Matter [51]; bottom right: Falk and Kelemen [31].

3. Carbon mass transfer in subduction zones

Fully carbonated peridotites (listvenites) are exposed along the basal thrusts of some ophiolites, including the Samail ophiolite, which is a block of oceanic crust and upper mantle in Oman and the UAE that was emplaced along the Arabian continental margin about 70 million years ago [50]. For 25 million years prior to emplacement, the Samail ophiolite formed the hanging wall above a subduction zone, beneath which several hundred kilometers of oceanic crust and deep sea sediment were thrust into the mantle. Studies of the listvenites showed that they formed at $\sim 100^\circ\text{C}$, by carbonation of the shallow, “leading edge of the mantle wedge”, with CO_2 supplied by fluids generated from decarbonation of the underlying, subducting sediments [31]. In 2017, Hole BT1B of the Oman Drilling Project sampled 200 meters of listvenite and serpentinite, the basal thrust fault (former subduction zone), and 100 meters of underlying metamorphosed sediments. Preliminary results from core analysis include evidence for generation of CO_2 -bearing aqueous fluids from subducting sediments at higher temperature and pressure, followed by unmixing of the ascending, cooling fluid into H_2O -rich and CO_2 -rich, immiscible components that formed different mineral assemblages within the listvenites [3–7]. In the context of potential, engineered in situ carbon mineralization, the primary relevance of these results is that 100% peridotite carbonation can be achieved at moderate temperatures and CO_2 partial pressures.

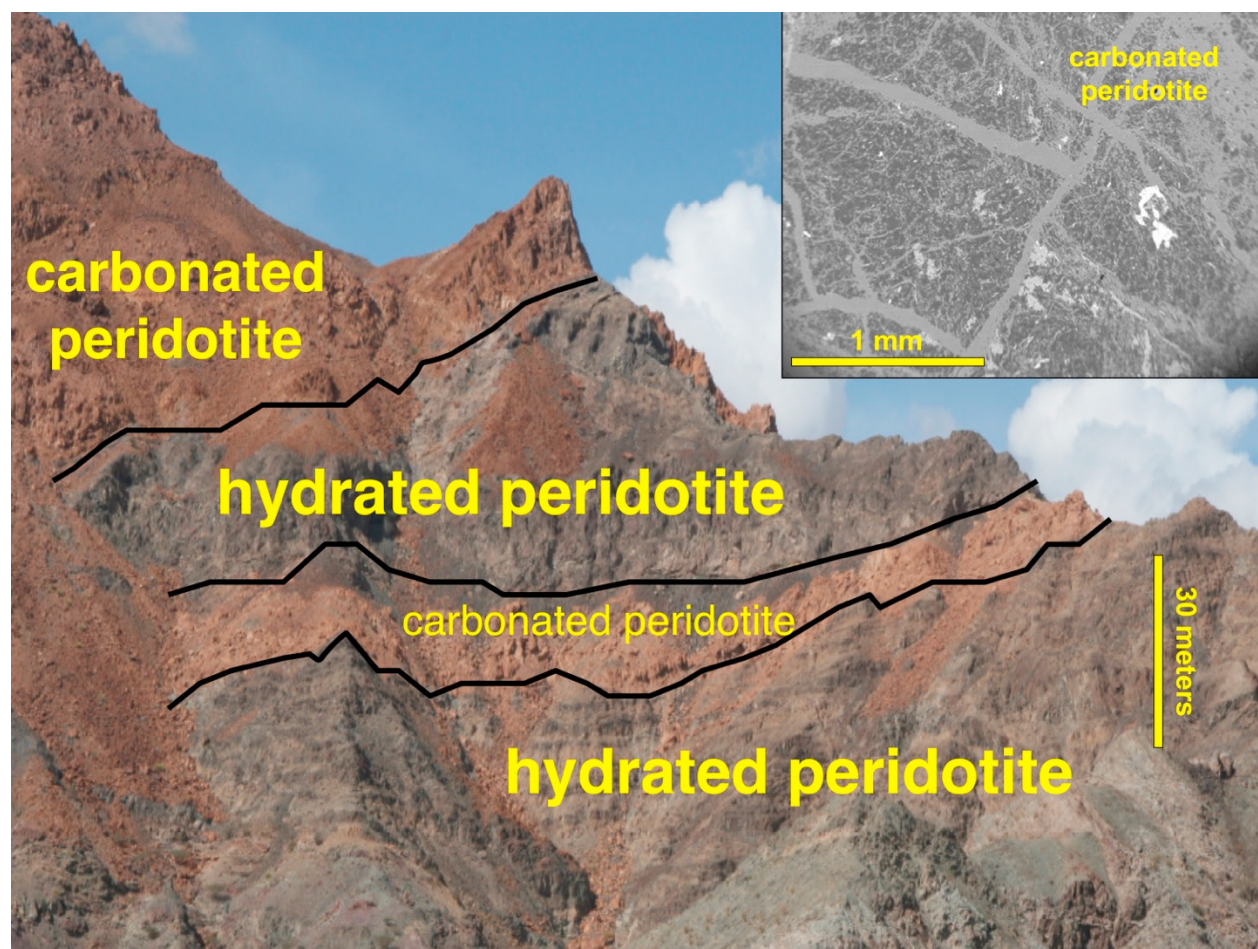


Fig. 2. Red bands of fully carbonated peridotite (listvenite) in green-grey partially serpentinitized mantle peridotite in Oman. Inset is a back-scattered electron image of listvenite, in which dark grey areas are magnetite (MgCO_3), light grey areas are quartz (SiO_2) and bright grey and white areas are Cr-rich oxide minerals. Modified from Falk and Kelemen [31].

4. Laboratory and theoretical investigations of the pressure of crystallization and reaction-driven cracking

Kelemen and Matter [51], Rudge et al. [52], Kelemen et al. [26], Kelemen and Hirth [53] and Evans et al. [17] proposed that large increases in the solid volume during peridotite serpentinization and carbonation might lead to “reaction-driven cracking” (aka reactive cracking). Volume increases within an elastic container produce stress, known as the pressure of crystallization, which can lead to fracture formation, in a positive feedback mechanism that maintains or enhances permeability, fluid flow, and reactive surface area. We pointed to previous and concurrent work on cracking caused by serpentinization [15, 16, 54–57], by “salt weathering” (reviews in [58–60]), and by reaction-driven cracking in general (e.g., [61–63]). The overall concept seems simple enough, and reaction-driven cracking has been observed in peridotite carbonation experiments [64], as well as analog experiments on hydration of periclase (MgO) to produce brucite ($\text{Mg}(\text{OH})_2$) [12]. Other analog experiments have demonstrated that significant crystallization pressures are generated by hydration of lime (CaO) to form portlandite ($\text{Ca}(\text{OH})_2$) (up to 153 MPa, [8, 11]) and of basanite ($\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) to produce gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [9]. In the latter case crystallization pressure is limited due to stress relaxation via viscous creep of weak gypsum. Similarly, frictional yielding of brucite at ~ 30 MPa [65–67] may limit the maximum stress in the experiments of Zheng et al. [12].

In other experimental tests of olivine carbonation and hydration, volume change and fractures were not observed [10], and permeability dropped with increasing reaction progress [68–73]. The reasons for these varied experimental results are not yet clear. It is becoming apparent that micro- and nano-scale properties of fluid-rock systems, such as fluid-mineral surface energy, and related characteristics such as sorptivity and disjoining pressure [8, 12, 17, 58, 74, 75] may play a significant role in locating the crucial bifurcation between self-limiting negative feedbacks (clogging) and accelerating, positive feedbacks (cracking). Other processes, for example, selective, local dissolution and precipitation processes and/or crack propagation from etch pits along dislocation boundaries and other defects in olivine crystals [49, 72, 73, 76–82] – may also play a role in sustaining permeability and fluid flow. Perhaps, complete carbonation in natural systems is relatively slow, and thus cannot be engineered on a human time scale, as suggested by Van Noort et al. [10]. However, in the competition between (i) volume expansion and stress accumulation, and (ii) processes that relax elastic stresses such as pressure solution or frictional sliding along existing fractures, it seems likely that reaction-driven cracking happens when the rates of reaction and volume change are maximized.

This is an active and fertile topic for ongoing research. Understanding positive and negative feedbacks between reaction and fluid flow is crucial for any applied method of in situ carbon mineralization, particularly in peridotite formations with limited initial porosity.

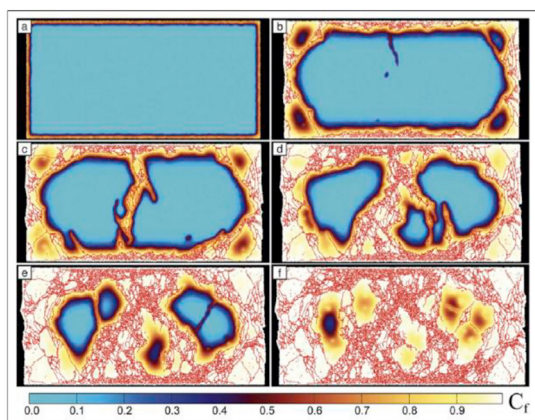


Fig. 3. Numerical model of reaction driven cracking from Royne et al. [13] in a rectangular block of rock surrounded by fluid in 2D. Blue rock reacts with surrounding black fluid to form white solid product, with volume increase and associated stress concentrations forming red cracks. In turn, red cracks provide rapid fluid access deeper into the block of rock. This discrete element model provides clear simulations of fracture formation at the grain scale, but does not incorporate Darcy flow within the porous fracture network.

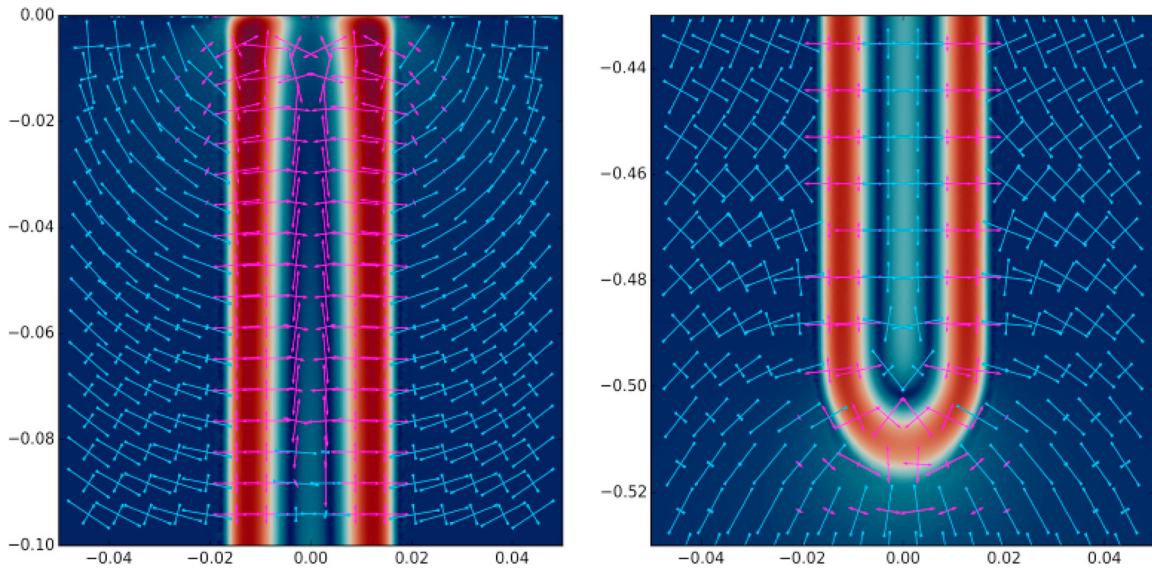


Fig. 4. From Evans et al. [17]. Non-dimensional stress magnitudes (colors) in 2D model of a tabular zone of high porosity infiltrated by CO_2 -rich fluid, reacting with olivine to produce carbonate minerals with volume expansion. The pink and blue arrows indicate tensile and compressive stresses respectively. These stress orientations should result in horizontal fractures, perpendicular to the initial, vertical zone of high porosity.



Fig. 5. From Evans et al [17]. White carbonate veins in partially serpentinized peridotite in, with the characteristic texture we call “ladder cracks” or “Frankenstein veins”. A central, carbonate vein is flanked by smaller, terminated, carbonate veins perpendicular to the central one.

5. Rate, cost and capacity of proposed methods for engineered carbon mineralization

Building upon our respective research programs, in response to requests by several groups reviewing methods for carbon dioxide removal from air (CDR), as well as associated CO₂ storage, a group of us (Aines, Benson, Dipple, Gadikota, Kelemen, Renforth, Wilcox) have compiled estimates of rates, reservoir capacities and costs of carbon mineralization in ultramafic rocks, in comparison with values for other proposed methods of CDR and CO₂ storage. We are now in the process of preparing papers on the results [18, 19]. These are not yet complete, and are the product of extensive literature review, so with apologies we will refrain from most citations, and limit the quantitative information shared here.

Some tentative highlights include: Mine tailings are the “low hanging fruit”, and can achieve CDR at costs much lower than manufactured air capture systems, as recently reviewed by, e.g., [83]). There is significant industry interest in applying carbon mineralization, for CDR and/or storage of CO₂ captured from point sources, at the Mt. Keith mine (e.g., [84]) and more generally by the DeBeers diamond-mining consortium [85]. However, the CO₂ uptake capacity of mine tailings (existing, and produced annually) is low compared to human emissions of CO₂ and other greenhouse gases. Mining and processing ultramafic rocks for the purpose of CDR + solid storage may be cost and capacity competitive with manufactured air capture systems + storage, within the uncertainties of estimates for both options. However, at rates of Gt CO₂/yr, these methods might generate unacceptable volumes of tailings. Dispersal of finely ground olivine and/or brucite in agricultural soils, along shorelines, or in the shallow oceans, may also be similar in cost and capacity to manufactured CDR systems, but rates are so low, reactants are so dispersed, and areas are so large that this has been difficult to assess quantitatively.

CO₂ storage via *in situ* carbon mineralization in ultramafic rock formations may be cost and capacity competitive with storage of supercritical CO₂ fluid in subsurface pore space. However, this depends on avoiding negative feedbacks due to “clogging” of pore space and armoring of reactive surfaces as discussed in Section 4, above. Positive feedback regimes may exist, for example via “reaction-driven cracking” driven by stress due to solid volume change during carbonate crystallization. This is a topic for continued, basic research.

CDR via circulation of surface water through subsurface ultramafic rocks is less likely to generate clogging and passivation, compared to circulation of CO₂-rich fluids, but could be economically feasible only where the geothermal gradient and permeability are sufficiently high for thermal convection. This is because the CO₂ concentration in water saturated in air is ~ 100 ppm, so \$0.01 spent pumping a mass of water is equivalent to \$100 for the same mass of CO₂. Instead or in addition, combined CDR and geothermal power generation is possible in some regions.

While experiments on the rate of dissolution and/or carbon mineralization via reaction of aqueous fluids with various rock materials are fairly numerous, comparisons are hindered because different experimental conditions were used with different rock reactants. Gadikota et al. [18] performed a direct comparison of carbonation rates for olivine, plagioclase, basalt, and anorthosite (gabbro) with the same P, T, duration, and fluid composition, and similar grain sizes. These experiments confirmed that olivine undergoes more rapid carbonation than the other materials. Addition of NaHCO₃ increases carbonation rates for several of these materials (though in natural systems buffering of pH by water/rock reaction may have a similar effect). While most rock materials undergo passivation and decreasing reaction rates with increasing reaction progress, in most cases experimental olivine carbonation rates are approximately constant to more than 90% completion [18, 23, 25, 86]. This may be due to “reaction-driven cracking”, formation of etch pits, and/or other processes that continually renew olivine reactive surface area.

6. Conclusion

Study of *in situ* carbon mineralization in ultramafic rocks is an active field of basic and applied research. Work to date has identified many essential processes that are not well understood, which can form the basis for highly rewarding, continued investigation. Engineered methods that emulate spontaneous, natural systems could – in principle – harness the chemical potential energy inherent in disequilibrium between the atmosphere and tectonically exposed rocks from the Earth’s interior, thereby reducing cost and energy demands. However, such methods remain almost entirely speculative. A few small- to medium-scale pilot experiments, similar to the CarbFix and Wallula experiments on *in situ* carbon mineralization in basalt [87–96], would greatly advance knowledge and assessment of the feasibility of large-scale application of these ideas.

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References

- [1] de Obeso J.C., P.B. Kelemen, and J.A. Higgins. “Tracing alteration of mantle peridotite in the Samail ophiolite using Mg isotopes” *AGU Fall Meeting Abstracts* (2017): V34A-06.
- [2] de Obeso J.C., and P.B. Kelemen. “Geochemistry and petrology of altered peridotite overlain by Maastrichtian to Miocene sediments in the SE Samail Ophiolite, Oman” *AGU Fall Meeting Abstracts* (2015): V11A-3056.
- [3] Godard M., E. Bennett, E. Carte, F. Kourim? R. Lafay, J. Noël, et al. “Geochemical and Mineralogical Profiles Across the Listvenite-Metamorphic Transition in the Basal Megathrust of the Oman Ophiolite: First Results from Drilling at Oman Drilling Project Hole BT1B” (2017): 328591.
- [4] Kelemen P.B., M. Godard, K.T.M. Johnson, K. Okazaki, C.E. Manning, J.L. Urai, et al. “Peridotite carbonation at the leading edge of the mantle wedge: OmDP Site BT1” *AGU Fall Meeting Abstracts* (2017): 328655.
- [5] de Obeso J.C., P.B. Kelemen, C.E. Manning, K. Michibayashi, M. Harris, and Party ODPPS. “Listvenite formation from peridotite: Insights from Oman Drilling Project hole BT1B and preliminary reaction path model approach” *AGU Fall Meeting Abstracts* (2017): 328802.
- [6] Manning C.E., P.B. Kelemen, K. Michibayashi, M. Harris, J.L. Urai, J.C. de Obeso, et al. “Transformation of serpentinite to listvenite as recorded in the vein history of rocks From Oman Drilling Project Hole BT1B” *AGU Fall Meeting Abstracts* (2017): 328604.
- [7] Morishita T., P.B. Kelemen, J.A. Coggon, M. Harris, J.M. Matter, K. Michibayashi, et al. “Drilling the leading edge of the mantle wedge and the underlying metamorphic sole of the Samail Ophiolite: Hole BT1B, Oman Drilling Project” *AGU Fall Meeting Abstracts* (2017): 328828.
- [8] Lambert S., H.M. Savage, and P.B. Kelemen. “Experimental investigation of the pressure of crystallization of $\text{Ca}(\text{OH})_2$: Implications for the reactive-cracking process” *G-cubed* (2018), submitted.
- [9] Skarbek R., H. Savage, and P.B. Kelemen. “Competition between crystallization-induced expansion and creep compaction during gypsum formation” *J. Geophys. Res.* (2018), accepted.
- [10] van Noort R., T.K.T. Wolterbeek, M.R. Drury, M.T. Kandianis, and C.J. Spiers. “The force of crystallization and fracture propagation during in-situ carbonation of peridotite” *Minerals* 7 (2017), doi:10.3390/min7100190.
- [11] Wolterbeek T.K.T., R. van Noort, and C.J. Spiers. „Reaction-driven casing expansion: potential for wellbore leakage mitigation” *Acta Geotech.* (2017), doi:10.1007/s11440-017-0533-5.
- [12] Zheng X., B. Cordonnier, W. Zhu, F. Renard, and B. Jamtveit. “Effects of confinement on reaction-induced fracturing during hydration of periclase” *G-cubed* (2018), in review.
- [13] Royne A., B. Jamtveit, J. Mathiesen, and A. Malthe-Sorensen. “Controls on rock weathering rates by reaction-induced hierarchical fracturing” *Earth and Planetary Science Letters* 275 (2008): 364-369.
- [14] Rudge J.F., P.B. Kelemen, and M. Spiegelman. “A simple model of reaction-induced cracking applied to serpentinization and carbonation of peridotite” *Earth and Planetary Science Letters* 291 (2010): 215-27.
- [15] Ulven O.I., B. Jamtveit, and A. Malthe-Sorensen. “Reaction driven fracturing of porous rocks” *Journal of Geophysical Research* 119 (2014), doi:10.1002/2014JB011102.
- [16] Ulven O.I., H. Storheim, H. Austrheim, and A. Malthe-Sorensen. “Fracture initiation during volume increasing reactions in rocks and applications for CO_2 sequestration” *Earth and Planetary Science Letters* 389 (2014): 132-142.
- [17] Evans O., M.W. Spiegelman, and P.B. Kelemen. “Reactive-brittle dynamics in peridotite alteration” *Journal of Geophysical Research* (2018), in review.
- [18] Gadikota G., J.M. Matter, P.B. Kelemen, P.V. Brady, A.-H.A. Park. “Comparison of the carbon mineralization behavior of labradorite, anorthosite and basalt for CO_2 storage” (2018), in preparation.
- [19] Kelemen P.B., P. Renforth, G.M. Dipple, G. Gadikota, J. Wilcox, S.M. Benson, et al. “Review of rates, cost and capacity of carbon mineralization in ultramafic rocks” *2nd De Beers Mineral Carbonation Workshop Abstract* (2018), in press.
- [20] Kelemen P.B., and C.E. Manning. “Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up” *PNAS* 112 (2015): E3997-E4006, doi:10.1073/pnas.1507889112.
- [21] Seifritz W. “ CO_2 disposal by means of silicates” *Nature* 345 (1990): 486.
- [22] Lackner K.S., C.H. Wendt, D.P. Butt, E.L. Joyce, and D.H. Sharp. “Carbon-dioxide disposal in carbonate minerals” *Energy* 20 (1995): 1153-1170.
- [23] O'Connor W.K., D.C. Dahlin, G.E. Rush, S.J. Gerdemann, and D.N. Nilsen. “Final report: Aqueous mineral carbonation, DOE/ARC-TR-04-002” Albany, OR: Office of Process Development, Albany Research Center, Office of Fossil Energy, US DOE (2004).
- [24] Chizmeshya A.V.G., M.J. McKelvy, K. Squires, R.W. Carpenter, and H. Béarat. “DOE Final Report 924162: A novel approach to mineral carbonation: Enhancing carbonation while avoiding mineral pretreatment process cost” Tempe, AZ: Arizona State University (2007).
- [25] Gadikota G., J.M. Matter, P.B. Kelemen, AND A.-H.A. Park. “Chemical and morphological changes during olivine carbonation for CO_2 storage in the presence of NaCl and NaHCO_3 ” *Physical Chemistry Chemical Physics* 16 (2014): 4679-4693.
- [26] Kelemen P.B., J.M. Matter, E.E. Streit, J.F. Rudge, W.B. Curry, and J. Bluztaj. “Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO_2 capture and storage” *Annual Review of Earth and Planetary Sciences* 39 (2011): 545-576.

- [27] Beinlich A., H. Austrheim, J. Glodny, M. Erambert, T.B. Andersen. "CO₂ sequestration and extreme Mg depletion in serpentinized peridotite clasts from the Devonian Solund basin, SW-Norway" *Geochimica et Cosmochimica Acta* 74 (2010): 6935-6964.
- [28] Beinlich A., O. Plummer, J. Hovelmann, H. Austrheim, and B. Jamtveit. "Massive serpentinite carbonation at Linnajavri, N-Norway" *Terra Nova* 24 (2012): 446-455.
- [29] Beinlich A., V. Mavromatis, H. Austrheim, and E.H. Oelkers. "Inter-mineral Mg isotope fractionation during hydrothermal ultramafic rock alteration – Implications for the global Mg-cycle" *Earth and Planetary Science Letters* 392 (2014): 166-176.
- [30] Tominaga M., A. Beinlich, E.A. Lima, M.A. Tivey, B.A. Hampton, B. Weiss, et al. "Multi-scale magnetic mapping of serpentinite carbonation" *Nature Communications* 8 (2017), doi:10.1038/s41467-017-01610-4.
- [31] Falk E.S., and P.B. Kelemen. "Geochemistry and petrology of listvenite in the Oman Ophiolite: Complete carbonation of peridotite during ophiolite emplacement" *Geochimica et Cosmochimica Acta* 160 (2015): 70-90.
- [32] Falk E.S., W. Guo, A.N. Paukert, J.M. Matter, E.M. Mervine, and P.B. Kelemen. "Controls on the stable isotope compositions of travertine from hyperalkaline springs in Oman: Insights from clumped isotope measurements" *Geochimica et Cosmochimica Acta* 192 (2016): 1-28.
- [33] Streit E., P.B. Kelemen, and J. Eiler. "Coexisting serpentine and quartz from carbonate-bearing serpentinized peridotite in the Samail Ophiolite, Oman" *Contributions to Mineralogy and Petrology* 164 (2012): 821-837.
- [34] Paukert A.N., J.M. Matter, P.B. Kelemen, E.L. Shock, and J.R. Havig. "Reaction path modeling of enhanced in situ CO₂ mineralization for carbon sequestration in the peridotite of the Samail Ophiolite, Sultanate of Oman" *Chemical Geology* 330 (2012): 86-100.
- [35] Mervine E.M., S.E. Humphris, K.W.W. Sims, P.B. Kelemen, and W.J. Jenkins. "Carbonation rates of peridotite in the Samail Ophiolite, Sultanate of Oman constrained through 14C dating and stable isotopes" *Geochimica et Cosmochimica Acta* 126 (2014): 371-397.
- [36] Mervine E.M., K.W.W. Sims, S.E. Humphris, and P.B. Kelemen. "Applications and limitations of U-Th disequilibria systematics for determining rates of peridotite carbonation in the Samail Ophiolite, Sultanate of Oman" *Chemical Geology* 412 (2015): 151-166.
- [37] Chavagnac V., C. Monnin, G. Ceuleneer, C. Boulart, and G. Hoareau. "Characterization of hyperalkaline fluids produced by low-temperature serpentinization of mantle peridotites in the Oman and Ligurian ophiolites" *G-cubed* 14 (2013): 2496-2522.
- [38] Chavagnac V., G. Ceuleneer, C. Monnin, B. Lansac, G. Hoareau, and C. Boulart. "Mineralogical assemblages forming at hyperalkaline warm springs hosted on ultramafic rocks: a case study of Oman and Ligurian ophiolites" *G-cubed* 14 (2013): 2474-2495.
- [39] Monnin C., V. Chavagnac, C. Boulart, B. Ménez, M. Gérard, E. Gérard, et al. "Fluid chemistry of the low temperature hyperalkaline hydrothermal system of Prony Bay (New Caledonia)" *Biogeosciences* 11 (2014): 5687-5706.
- [40] Quesnel B., P. Gautier, P. Boulvais, M. Cathelineau, P. Maurizot, D. Cluzel, et al. "Syn-tectonic, meteoric water-derived carbonation of the New Caledonia peridotite nappe" *Geology* 41 (2013): 1063-1066.
- [41] Ulrich M., M. Munoz, S. Guillot, M. Cathelineau, C. Picard, B. Quesnel, et al. "Dissolution-precipitation processes governing the carbonation and silicification of the serpentinite sole of the New Caledonia ophiolite" *Contributions to Mineralogy Petrology* 167 (2014): 952, doi:10.1007/s00410-013-0952-8.
- [42] Quesnel B., P. Boulvais, P. Gautier, M. Cathelineau, C.M. John, M. Dierick, et al. "Paired stable isotopes (O, C) and clumped isotope thermometry of magnesite and silica veins in the New Caledonia Peridotite Nappe" *Geochimica et Cosmochimica Acta* 183 (2016): 234-249.
- [43] Garcia del Real P., K. Maher, T. Kluge, D.K. Bird, G.E. Brown, and C.M. John. "Clumped-isotope thermometry of magnesium carbonates in ultramafic rocks" *Geochimica et Cosmochimica Acta* 193 (2016): 222-250.
- [44] Miller H.M., J.M. Matter, P.B. Kelemen, E.T. Ellison, M. Conrad, N. Fierer, et al. "Modern water/rock reactions in Oman hyperalkaline peridotite aquifers and implications for microbial habitability" *Geochimica et Cosmochimica Acta* 179 (2016): 217-241.
- [45] Rempfort K.R., H.M. Miller, N. Bompard, D. Nothaft, J.M. Matter, P.B. Kelemen, N. Fierer, and A.S. Templeton. "Geological and geochemical controls on subsurface microbial life in the Samail Ophiolite, Oman" *Frontiers in Microbiology* (2017): Article 56.
- [46] Mayhew L.E., E.T. Ellison, H.M. Miller, P.B. Kelemen, and A.S. Templeton. "Iron transformations during low temperature alteration of variably serpentinized rocks from the Samail ophiolite, Oman" *Geochimica et Cosmochimica Acta* 222 (2018): 704-728.
- [47] Scott S., K.W. Sims, B.R. Frost, P.B. Kelemen, K.A. Evans, and S.M. Swapp. "On the hydration of olvine in ultramafic rocks: Implications for Fe isotopes in serpentinites" *Geochimica et Cosmochimica Acta* 215 (2017): 105-121.
- [48] Malvoisin B. "Mass transfer in the oceanic lithosphere: serpentinization is not isochemical" *Earth and Planetary Science Letters* 430 (2015): 75-85.
- [49] Rouméjon S., and M. Cannat. "Serpentinization of mantle-derived peridotites at mid-ocean ridges: Mesh texture development in the context of tectonic exhumation" *G-cubed* 15 (2014): 2354-2379.
- [50] Nasir S., A.R. Al Sayigh, A. Al Harthy, S. Al-Khribash, O. Al-Jaaidi, A. Musllam, et al. "Mineralogical and geochemical characterization of listwaenite from the Semail ophiolite, Oman" *Chemie Der Erde* 67 (2007): 213-228.
- [51] Kelemen P.B., and J.M. Matter. "In situ carbonation of peridotite for CO₂ storage" *PNAS* 105 (2008): 17,295-17,300.
- [52] Rudge J.F., P.B. Kelemen, and M. Spiegelman. "A simple model of reaction induced cracking applied to serpentinization and carbonation of peridotite" *Earth and Planetary Science Letters* 291 (2010): 215-227.
- [53] Kelemen P.B., and G. Hirth. "Reaction-driven cracking during retrograde metamorphism: Olivine hydration and carbonation" *Earth and Planetary Science Letters* 345-348 (2012): 81-89.
- [54] MacDonald A.H., and W.S. Fyfe. "Rate of serpentinization in seafloor environments" *Tectonophysics* 116 (1985): 123-135.
- [55] O'Hanley D.S. "Solution to the volume problem in serpentinization" *Geology* 20 (1992): 705-708.
- [56] Iyer K., B. Jamtveit, J. Mathiesen, A. Malthe-Sørenssen, and J. Feder. "Reaction-assisted hierarchical fracturing during serpentinization" *Earth and Planetary Science Letters* 267 (2008): 503-516.
- [57] Malvoisin B., N. Brantut, and M.-A. Kaczmarek. "Control of serpentinization rate by reaction-induced cracking" *Earth and Planetary Science Letters* 476 (2017): 143-152.
- [58] Scherer G.W. "Stress from crystallization of salt" *Cement and Concrete Research* 34 (2004): 1613-1624.

- [59] Steiger M. “Crystal growth in porous materials – I: The crystallization pressure of large crystals” *Journal of Crystal Growth* 282 (2005): 455-469.
- [60] Steiger M. “Crystal growth in porous materials – II: Influence of crystal size on the crystallization pressure” *Journal of Crystal Growth* 282 (2005): 470-481.
- [61] Malthé-Sorensen A., B. Jamtveit, and P. Meakin. “Fracture patterns generated by diffusion controlled volume changing reactions” *Physical Review Letters* 96 (2006): 245501-1 to 4.
- [62] Jamtveit B., C. Putnis, and A. Malthé-Sorensen. “Reaction induced fracturing during replacement processes” *Contributions to Mineralogy and Petrology* 157 (2009): 127-133.
- [63] Røyne A., and D.K. Dysthe. “Rim formation on crystal faces growing in confinement” *Journal of Crystal Growth* 346 (2012): 89-100.
- [64] Zhu W., F. Fusseis, H. Lisabeth, T. Xing, X. Xiao, V. De Andrade, et al. “Experimental evidence of reaction-induced fracturing during olivine carbonation” *Geophysical Research Letters* 43 (2016): 9535-9543.
- [65] Morrow C.A., D.E. Moore, and D.A. Lockner. “The effect of mineral bond strength and adsorbed water on fault gouge frictional strength” *Geophysical Research Letters* 27 (2000): 815-818.
- [66] Moore D.E., and D.A. Lockner. “Crystallographic controls on the frictional behavior of dry and water-saturated sheet structure minerals” *Journal of Geophysical Research* 109 (2004).
- [67] Moore D.E., and D.A. Lockner. “Comparative deformation behavior of minerals in serpentinized ultramafic rock: Application to the slab-mantle interface in subduction zones” *International Geology Review* 49 (2007): 401-415.
- [68] Andreani M., L. Luquot, P. Gouze, M. Godard, E. Hoisé, and B. Gibert. “Experimental study of carbon sequestration reactions controlled by the percolation of CO₂-rich brine through peridotites” *Environmental Science & Technology* 43 (2009): 1226-1231.
- [69] Hövelmann J., H. Austrheim, and B. Jamtveit. “Microstructure and porosity evolution during experimental carbonation of a natural peridotite” *Chemical Geology* 334 (2012): 254–265.
- [70] Godard M., L. Luquot, M. Andreani, and P. Gouze. “Incipient hydration of mantle lithosphere at ridges: A reactive-percolation experiment” *Earth and Planetary Science Letters* 371-372 (2013): 92-102.
- [71] Farough A., D.E. Moore, D.A. Lockner, and R.P. Lowell. “Evolution of fracture permeability of ultramafic rocks undergoing serpentinization at hydrothermal conditions: An experimental study” *G-cubed* 17 (2016): 44-55.
- [72] Lisabeth H.P., W. Zhu, P.B. Kelemen, and A. Ilgen. “Experimental evidence for chemo-mechanical coupling during carbon mineralization in ultramafic rocks” *Earth and Planetary Science Letters* 474 (2017): 355-367.
- [73] Peuble S., M. Andreani, P. Gouze, M. Pollet-Villard, B. Reynard, and B. Van de Moortele. “Multi-scale characterization of the incipient carbonation of peridotite” *Chemical Geology* 476 (2018): 150-160.
- [74] Renard F. “Microfracturation in rocks: from microtomography images to processes” *The European Physical Journal Applied Physics* 60 (2012).
- [75] Røyne A., and B. Jamtveit. “Pore-scale controls on reaction-driven fracturing” *Reviews in Mineralogy and Geochemistry* 80 (2015): 25-44.
- [76] Velbel M.A. “Dissolution of olivine during natural weathering” *Geochimica et Cosmochimica Acta* 73 (2009):6098-6113.
- [77] Daval D., O. Sissmann, N. Menguy, G.D. Saldi, F. Guyot, I. Martinez, et al. “Influence of amorphous silica layer formation on the dissolution rate of olivine at 90 °C and elevated pCO₂” *Chemical Geology* 284 (2011): 193-209.
- [78] Plümper O., A. Royné, A. Magraso, and B. Jamtveit. “The interface-scale mechanism of reaction-induced fracturing during serpentinization” *Geology* 40 (2012): 1103-1106.
- [79] Klein F., N.G. Grozeva, J.S. Seewald, T.M. McCollom, S.E. Humphris, B. Moskowitz, et al. “Fluids in the crust: Experimental constraints on fluid-rock reactions during incipient serpentinization of harzburgite” *American Mineralogist* 100 (2015): 991-1002.
- [80] Grozeva N.G., F. Klein, J.S. Seewald, and S.P. Sylva. “Experimental study of carbonate formation in oceanic peridotite” *Geochimica et Cosmochimica Acta* 199 (2017): 264-286.
- [81] McCollom T.M., F. Klein, M. Robbins, B. Moskowitz, T.S. Berquó, N. Jöns, et al. “Temperature trends for reaction rates, hydrogen generation, and partitioning of iron during experimental serpentinization of olivine” *Geochimica et Cosmochimica Acta* 181 (2016): 175-200.
- [82] Lisabeth H., W. Zhu, T. Xing, and V. De Andrade. “Dissolution-assisted pattern formation during olivine carbonation” *Geophysical Research Letters* 44 (2017), doi:10.1002/2017GL074393.
- [83] Power I.M., A.L. Harrison, G.M. Dipple, S.A. Wilson, P.B. Kelemen, M. Hitch, et al. “Carbon mineralization: From natural analogues to geoengineered systems” *Reviews in Mineralogy and Geochemistry* 77 (2013): 305-360.
- [84] Wilson S.A., A.L. Harrison, G.M. Dipple, I.M. Power, S.L.L. Barker, K.U. Mayer, et al. “Offsetting of CO₂ emissions by air capture in mine tailings at the Mount Keith Nickel Mine, Western Australia: Rates, controls and prospects for carbon neutral mining” *International Journal of Greenhouse Gas Control* 25 (2014): 121-140.
- [85] Mervine E.M., G.M. Dipple, I.M. Power, S.A. Wilson, G. Southam, C. Southam, et al. “Potential for offsetting diamond mine carbon emissions through mineral carbonation of processed kimberlite” *11th International Kimberlite Conference Abstracts* (2017): 11IKC-4553.
- [86] Eikeland E., A.B. Blichfeld, C. Tyrsted, A. Jensen, and B.B. Iversen. “Optimized carbonation of magnesium silicate mineral for CO₂ storage” *ACS Applied Materials and Interfaces* 7 (2015): 5258-5264.
- [87] Gislason S.R., D. Wolff-Boenisch, A. Stefansson, E.H. Oelkers, E. Gunnlaugsson, H. Sigurdardottir, et al. “Mineral sequestration of carbon dioxide in basalt: The CarbFix project” *International Journal of Greenhouse Gas Control* 4 (2010): 537-545.
- [88] Aradottir E.S.P., H. Sigurdardottir, B. Sigfusson, and E. Gunnlaugsson. “CarbFix: A CCS pilot project imitating and accelerating natural CO₂ sequestration” *Greenhouse Gases - Science and Technology* 1 (2011): 105-118.
- [89] Matter J.M., W. Broecker, S.R. Gislason, E. Gunnlaugsson, E.H. Oelkers, M. Stute, et al. “The CarbFix Pilot Project: Storing carbon dioxide in basalt” *Energy Procedia* 4 (2011): 5579-5585.

- [90] Matter J.M., M. Stute, S.Ó. Snæbjörnsdóttir, E.H. Oelkers, S.R. Gislason, E.S.P. Aradóttir, et al. “Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions” *Science* 352 (2016): 1312-1314.
- [91] Snæbjörnsdóttir S.Ó., E.H. Oelkers, K. Mesfin, E.S. Aradóttir, K. Dideriksen, I. Gunnarsson, et al. “The chemistry and saturation states of subsurface fluids during the in situ mineralisation of CO₂ and H₂S at the CarbFix site in SW-Iceland” *International Journal of Greenhouse Gas Control* 58 (2017): 87-102.
- [92] Gunnarsson I., E.S.P. Aradóttir, E.H. Oelkers, D.E. Clark, M.P. Arnarsson, B. Sigfússon, et al. “The rapid and cost-effective capture and subsurface mineral storage of carbon and sulfur at the CarbFix site” (2018), in review.
- [93] McGrail B.P., F.A. Spane, J.E. Amonette, C.R. Thompson, and C.F. Brown. “Injection and monitoring at the Wallula Basalt Pilot Project” *Energy Procedia* 63 (2014): 2939-2948.
- [94] McGrail B.P., H.T. Schaef, F.A. Spane, J.A. Horner, A.T. Owen, J.B. Cliff, et al. “Wallula Basalt Pilot Demonstration Project: Post-injection results and conclusions” *Energy Procedia* 114 (2017): 5783-5790.
- [95] McGrail B.P., H.T. Schaef, A.M. Ho, Y.-J. Chien, J.J. Dooley, and C.L. Davidson. “Potential for carbon dioxide sequestration in flood basalts” *Journal of Geophysical Research* 111 (2006): B12201, doi:10.1029/2005JB004169.
- [96] McGrail B.P., H.T. Schaef, F.A. Spane, J.B. Cliff, O. Qafoku, J.A. Horner, et al. “Field validation of supercritical CO₂ reactivity with basalts” *Environmental Science & Technology Letters* 4 (2017): 6-10.